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**PATENT ABSTRACTS OF JAPAN**

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**(54) CARBONACEOUS POROUS BODY AND ITS MANUFACTURING METHOD**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide an electrode for fuel cell which is excellent in gas diffusion, gas permeability, electric conductivity and flexibility.

**SOLUTION:** This carbonaceous porous body is substantially of pure carbon porous sheet with  $\leq 1$  mm to  $\geq 0.05$  mm thickness, and is flexible enough to be allowed to wind into cylinder of  $\leq 2$  cm diameter without break.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The carbonaceous porous material field excellent in the flexibility which is a with a 0.05 1mm or lessmm or more thickness [ which consists only of carbon substantially ] porous material sheet-like object, and is characterized by not destroying even if it winds around a cylinder-like object with an outer diameter of 20cm or less.

[Claim 2] The carbonaceous porous body according to claim 1 to which an air pressure is characterized by the air permeability at the time of fixed being [ the volume resistivities of the sheet thickness orientation ] below 0.1ohm and cm 10cm3 / (cm2 and s) above by 124Pa.

[Claim 3] The manufacture technique of the carbonaceous porous material field of having the property according to claim 1 or 2 characterized by sinking thermosetting resin into the nonwoven fabric which makes acrylonitrile system fire-resistance fiber main constituents, and processing at the temperature of 1300 degrees C or more among an inert atmosphere.

[Claim 4] The manufacture technique of the carbonaceous porous material field of having the property according to claim 1 or 2 characterized by sinking in and processing thermosetting resin at the temperature of 1300 degrees C or more among an inert atmosphere again after processing the nonwoven fabric which makes acrylonitrile system fire-resistance fiber main constituents at the temperature of 1300 degrees C or more among an inert atmosphere.

[Claim 5] The manufacture technique of the carbonaceous porous material field according to claim 3 or 4 characterized by using what processed the nonwoven fabric which makes acrylonitrile system fire-resistance fiber main constituents by the needle punch method and/or the stream confounding method.

[Claim 6] The manufacture technique of the carbonaceous porous material of the claim 4-5 characterized by using what created, using acrylonitrile system fire-resistance-ized fiber with a fiber length of 25-100mm as a nonwoven fabric made from acrylonitrile system fire-resistance-ized fiber given in any one term.

[Claim 7] Electrode material for fuel cells which consists of a carbonaceous porous material of the claim 1 or the claim 3 given in any one term.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

**[0001]**

[The technical field to which invention belongs] this invention relates to the carbonaceous porous material field suitable as an electrode material, especially a solid-state macromolecule type fuel cell gaseous diffusion layer, and its manufacture technique.

**[0002]**

[Description of the Prior Art] A diffusion and the permeability of the matter which participates in electrode reaction in addition to a current collection function are required of the electrode for solid-state macromolecule type fuel cells. Moreover, the intensity which is equal to the compression when constructing the intensity for it being equal to conductivity, gaseous diffusion and permeability, and a handling, and the time of an electrode manufacture and an electrode is needed for the material which constitutes the current collection field.

**[0003]** Thermosetting resin is infiltrated into the sheet-like precursor which consists of a carbon staple fiber like JP,9-157052,A as a process of such electrode material for solid-state macromolecule type fuel cells, and the technique of carbonizing is raised. For example, the technique which distributes underwater the carbon fiber cut into 6mm length grade with binders, such as polyvinyl alcohol, is immersed into a phenol resin solution in this precursor after forming a sheet-like precursor by the so-called paper-making technique pulled up on the screen, and is carbonized at the elevated temperature of about 2000 degrees C of inert atmospheres after xeraxis and resin hardening is common.

**[0004]** However, the carbide produced by such technique had the trouble where flexibility required since the fiber length of the carbon fiber to use is short, in order to roll round on a roll etc. was bad. Furthermore, it originates in fiber length being short, and was hard to raise the conductivity of the thickness orientation of sheet-like carbide. Moreover, in order to raise conductivity, when the compression press was carried out, the rate of a hole fell in the thickness orientation of a sheet-like object, and there was a problem that gas permeability became bad.

**[0005]**

[Problem(s) to be Solved by the Invention] this invention conquers the above troubles, is excellent in gaseous diffusion, permeability, and conductivity, and aims at offering the electrode for fuel cells which has flexibility further.

**[0006]**

[Means for Solving the Problem] As a result of this invention persons' inquiring zealously in view of the above-mentioned technical problem, it came to develop the carbonaceous porous material field which is a with a 0.05 1mm or lessmm or more thickness [ which consists only of carbon substantially ] porous material sheet-like object, and is characterized by not destroying even if it winds around a cylinder-like object with an outer diameter of 20cm or less.

**[0007]**

[Embodiments of the Invention] this invention is explained still in detail below.

**[0008]** Since the permeability of gas is demanded when using the carbonaceous porous body of this invention as a solid-state macromolecule type fuel cell electrode, it is desirable that the rate of a volume hole is 50% or more. Sinking thermosetting resin into the nonwoven fabric which makes polyacrylonitrile system fire-resistance fiber main constituents, and processing at the temperature of 1300 degrees C or more among an inert atmosphere as an example of the manufacture technique of this carbonaceous porous body, is mentioned. Moreover, after processing the nonwoven fabric which makes polyacrylonitrile system fire-resistance fiber main constituents at the temperature of 1300 degrees C or more among an inert atmosphere, it can make also by sinking in and processing thermosetting resin at the temperature of 1300 degrees C or more among an inert atmosphere again.

**[0009]** It is desirable that the orientation to the thickness orientation of a nonwoven fabric can be raised by using the needle punch method and/or a stream confounding method in case of a creation of the nonwoven fabric which makes polyacrylonitrile system fire-resistance fiber main constituents. In addition, it is rare to give a damage to fiber compared with the needle punch method, and production of the nonwoven fabric of a split is possible for the stream confounding method, and it is desirable.

**[0010]** (polyacrylonitrile system fire-resistance fiber) As for the polyacrylonitrile system fire-resistance fiber used for this invention, what fire-resistance-ization-processed the polyacrylonitrile system fiber of single-yarn fineness 0.5 - 3.3dtex by well-known technique is desirable. Moreover, it is desirable to use what carried out \*\*\*\* processing of the above-mentioned polyacrylonitrile system fire-resistance fiber, and was cut into about 25-100mm as a raw material of a polyacrylonitrile system fire-resistance fiber nonwoven fabric faced and used for carrying out this invention. The nonwoven fabric created using writing \*\*\*\*\* fire-resistance-ized fiber can fully raise the confounding between fiber by needle punch processing and stream confounding processing.

**[0011]** (The carbonization technique) A fire-resistance fiber nonwoven fabric or the fire-resistance fiber nonwoven fabric after resin sinking in, and the above-mentioned carbon fiber nonwoven fabric can do a carbonization by processing at an elevated temperature among an inert atmosphere. Although especially the technique is not limited, it is desirable to use the following technique, for example. A precursor is continuously thrown into the kiln which set up the linear temperature gradient substantially from 300 degrees C of the low-temperature sections to 800 degrees C of the elevated-temperature sections at a fixed speed from a low-temperature section side among the nitrogen ambient atmosphere. Take out 5 minutes after by the side of the elevated-temperature section, obtain a reserve carbon fiber nonwoven fabric, and this reserve carbon fiber nonwoven fabric is succeedingly supplied to the heating furnace of a

batch type. After carrying out a temperature up to 1300 degrees C or more at the rate of [ room temperature ] 10 degrees C/min after replacing by the nitrogen ambient atmosphere, and maintaining temperature about 1 hour at predetermined temperature, the temperature is lowered to a room temperature in 10 degrees C/min, and a carbonization nonwoven fabric is obtained. In addition, when an acrylonitrile system fiber precursor is used for a nonwoven fabric creation, fire-resistance-ized processing is required before carbonization processing. After are not limited to a batch type furnace, supplying a reserve carbon fiber nonwoven fabric continuously and processing fixed time especially as a format of the kiln which carries out the carbonization of the reserve carbon fiber nonwoven fabric, it is also possible to use the so-called continuous furnace which takes out a carbon fiber nonwoven fabric continuously. Moreover, as long as it does not necessarily limit to installing reserve carbonization kiln and carbonization kiln independently and it can secure a desired programming rate, reserve carbonization kiln and carbonization kiln may be united. Moreover, once processing a reserve carbonization temperature field, temperature is reset as a carbonization temperature field using the same kiln, and carbonization processing may be performed.

[0012] (thermosetting resin and the sinking-in technique) In order that it may be carbonized by calcinating and itself may play a role of a conductor, as for thermosetting resin, it is desirable to use the resin with high carbonization yield. As a compound carbonized, a polyacrylonitrile system polymer, a polyurethane system polymer, a phenol system resin, a furan system resin, a cellulose system high molecular compound, etc. are mentioned. The thermosetting resin used for this invention is the object in which tackiness or a fluidity is shown in ordinary temperature, and a phenol system resin, a furan system resin, etc. are used preferably. As a phenol system resin, the resol type phenol resin obtained by the reaction of a phenols and aldehydes can be used for the bottom of alkali catalyst presence. moreover, the self which contained the curing agent, for example, a hexamethylenediamine, in this case although lysis mixing of the phenol resin of the novolak type in which the heat weld nature of the solid-state which is generated by well-known technique to fluid resol type phenol resin, and is generated by the reaction of a phenols and aldehydes under an acid catalyst is shown could be carried out — bridge formation — it is desirable to use the thing of a type As a phenols, a phenol, a resorcinol, cresol, a xylol, etc. are used, for example. As aldehydes, formalin, a paraformaldehyde, a furfural, etc. are used, for example. Moreover, these can also be used as mixture. These can also use commercial elegance as phenol resin.

[0013] Although not limited especially as the resin sinking-in technique used for this invention, there are a dipping method and the nip method as general technique, a resin is melted to a solvent etc., and it is a deed about viscosity control. Subsequently, it is the technique of diving a fire-resistance fiber nonwoven fabric or a carbon fiber nonwoven fabric into a resin solution, and extracting a resin excessive subsequently with drawing equipment etc.

[0014] Moreover, the method of applying a direct resin to a fire-resistance fiber nonwoven fabric or a carbon fiber nonwoven fabric using a laminator etc. Or the technique of once film-izing a resin and imprinting after that to a fire-resistance fiber nonwoven fabric or a carbon fiber nonwoven fabric. Furthermore, a spray method can also be used when resin viscosity is comparatively low.

[0015]

[Example] Hereafter, an example explains this invention still in detail.

[0016] (winding in a cylinder-like object with an outer diameter of 20cm or less) It twisted more than a round so that a sample might be stuck to a paper tube with an outer diameter [ of 20cm ], and a bore of 15cm, and it observed whether a breakdown of a disconnection etc. would happen.

[0017] (measurement of air permeability) Permeability circuit tester Using FX3300 ( Switzerland by the tex test company), it measured 3 times about one sample, and the average was adopted as a permeability. The measuring-plane product was computed by 38cm<sup>2</sup> and 124Pa regularity of air pressures, and the unit was computed by cm<sup>3</sup>/(cm<sup>2</sup> and s).

[0018] (measurement of a volume resistivity)

1) Start a porous electrode base material to an abbreviation 30mmx30mm rectangle.

2) Measure the dimension and thickness (t) of length (l) and width (w) per 0.01mm using constant-pressure slide calipers.

3) The ten sheet laminating of the started porous electrode base material was carried out, it inserted and compressed with the copper plate of 50mm diameter and 10mm \*\*, inter-electrode resistance (Rohms) was measured using the ohm-meter, and it compressed and asked to the thickness from which a volume resistivity becomes the minimum value by the lower formula.

[0019]

[Equation 1]

$$\text{J体積抵抗率}(\Omega \cdot \text{cm}) = R \times l \times w / t \times 10$$

[0020] [The example of reference]

Acrylonitrile 96 mol%, (Manufacture of fire-resistance fiber and a carbon fiber nonwoven fabric) two mols % of methacrylic acids, and methyl-acrylate 2mol% — the precursor of single-yarn fineness 2.2dtx among the air ambient atmosphere by the acrylonitrile system polymer Heat-treated at the temperature of 230 degrees C - 280 degrees C, and obtained the fire-resistance fiber of 3 the density of 1.40g/cm. After having carried out crimp processing of this fiber by well-known technique, having considered as the staple fiber of 76mm of cut length, having made Webb by well-known technique subsequently and performing reserve needle punch processing, stream confounding processing was performed and the nonwoven fabric was obtained. Subsequently, after having carried out the temperature up to 1300 degrees C after having supplied the nonwoven fabric to the heating furnace of a batch type and replacing by the nitrogen ambient atmosphere, and maintaining temperature about 1 hour at this temperature, the temperature was lowered to the room temperature and the carbon fiber nonwoven fabric was obtained.

[0021] The coating was carried out to \*\*\*\*\* by the coating machine after deliquoring [example 1] phenol resin (\*\*\*\*\* light 5900. Dainippon Ink chemistry company make), and the phenol resin film was obtained. Subsequently, after having put 90g of eyes/, and the resin film of m2 on 120g of eyes/and the carbon fiber nonwoven fabric of m2 which were obtained in the example of reference and imprinting phenol resin, it inserted into the griddle which turned

the resin imprint side down and carried out the fluorine manipulation, and hardening of the phenol resin for [ every ] 10 minutes and under a carbon fiber nonwoven fabric and the air in a carbon fiber nonwoven fabric were removed under the temperature of 160 degrees C, and the condition of pressure 18MPa. Subsequently, after having inserted into the griddle which turned the resin imprint side up and carried out the fluorine manipulation after having put 90g of eyes/, and the resin film of m2 on the carbon fiber nonwoven fabric top and imprinting phenol resin and raising a pressure to the bottom of the temperature of 90 degrees C, and the condition of pressure 5MPa to 18MPa, subsequently every 2 minutes about room, the temperature up of the temperature was carried out to 170 degrees C, and hardening of for [ every ] 15 minutes and phenol resin was performed. Then, the electrode substrate was obtained by heating the above-mentioned interval base material for 1 hour, and carrying out a carbonization at 2000 degrees C, in the nitrogen gas ambient atmosphere. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0022] The electrode substrate was obtained like the example 1 except having used 60g of eyes/and the carbon fiber nonwoven fabric of m2 which were obtained in the example of [example 2] reference. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0023] 120g of eyes/and the carbon fiber nonwoven fabric of m2 which were obtained in the example of [example 3] reference are dipped in the 15 mass % ethanol solution of phenol resin (\*\*\*\*\* light 5900. Dainippon Ink chemistry company make), are pulled up, 75 weight section adhesion is carried out to the carbon fiber 100 weight section, after carrying out a reduced pressure drying at 60 degrees C for 2 hours, it inserted into the griddle which carried out the fluorine manipulation, and for 15 minutes and phenol resin were stiffened under 170 degrees C and the condition of pressure. Then, the electrode substrate was obtained by heating the above-mentioned interval base material for 1 hour, and carrying out a carbonization at 2000 degrees C, in the nitrogen gas ambient atmosphere. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0024] The electrode substrate was obtained like the example 3 except having used 60g of eyes/and the carbon fiber nonwoven fabric of m2 which were obtained in the example of [example 4] reference. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0025] The [example 1 of comparison] single-yarn fineness cut the fiber flux of the polyacrylonitrile system carbon fiber of 1.1dtexes, and the staple fiber whose mean fiber length is 6mm was obtained. Next, this fiber flux was \*\*\*\*\* underwater, the polyvinyl alcohol which is a binder was distributed uniformly at the fully distributed place, paper making was carried out, and 60g of eyes/and the carbon fiber paper of m2 were manufactured. A carbon fiber paper is dipped in the 15 mass % ethanol solution of phenol resin (\*\*\*\*\* light 5900. Dainippon Ink chemistry company make), is pulled up, 75 weight section adhesion is carried out to the carbon fiber 100 weight section, after carrying out a reduced pressure drying at 60 degrees C for 2 hours, it inserted into the griddle which carried out the fluorine manipulation, and for [ every ] 15 minutes and phenol resin were stiffened under 170 degrees C and the condition of pressure 18MPa. Then, the electrode substrate was obtained by heating the above-mentioned interval base material for 1 hour, and carrying out a carbonization at 2000 degrees C, in the nitrogen gas ambient atmosphere. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0026] The electrode substrate was obtained like the example 1 of a comparison except the hardening conditions of a carbon fiber paper of having infiltrated [example 2 of comparison] phenol resin being 15 minutes at pressure 21MPa and 170 degrees C. The result of thickness (mm) air permeability (cm<sup>3</sup>/(cm<sup>2</sup> and s)), a volume resistivity (ohm and cm), and a winding examination was shown in Table 1. [ of the obtained electrode substrate ]

[0027]

[Table 1]

	厚み (mm)	空気透過率 (cm <sup>3</sup> /cm <sup>2</sup> s)	体積抵抗率 (Ω・cm)	巻回試験
実施例1	0.32	10.6	0.078	破壊なし
実施例2	0.22	15.3	0.100	破壊なし
実施例3	0.30	10.1	0.081	破壊なし
実施例4	0.20	14.5	0.099	破壊なし
比較例1	0.16	18.0	0.120	破壊
比較例2	0.13	9.3	0.108	破壊

[0028]

[Effect of the Invention] It excelled in the conductivity of the thickness orientation by this invention, and it can be flexible and the suitable sheet-like porous-carbon material for a solid-state macromolecule type fuel cell electrode substrate strong also against bending can be offered now.

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最終頁に続く

(54) 【発明の名称】 炭素質多孔質体とその製造方法

(57) 【要約】

【課題】 ガス拡散、透過性、導電性に優れ、さらに柔軟性を有する燃料電池用電極の提供。

【解決手段】 実質的に炭素のみからなる厚さ1mm以下0.05mm以上の多孔質シート状物であって、外径20cm以下の円筒状物に巻回しても破壊しない柔軟性に優れた炭素質多孔質体。

## 【特許請求の範囲】

【請求項 1】 実質的に炭素のみからなる厚さ 1 mm 以下 0.05 mm 以上の多孔質シート状物であって、外径 20 cm 以下の円筒状物に巻回しても破壊しないことを特徴とする柔軟性に優れた炭素質多孔質体。

【請求項 2】 空気圧力が 124 Pa で一定時の空気透過率が  $10 \text{ cm}^3 / (\text{cm}^2 \cdot \text{s})$  以上、シート厚み方向の体積抵抗率が  $0.1 \Omega \cdot \text{cm}$  以下であることを特徴とする請求項 1 記載の炭素質多孔体。

【請求項 3】 アクリロニトリル系耐炎繊維を主要構成成分とする不織布に熱硬化性樹脂を含浸し、不活性雰囲気中 1300℃ 以上の温度で処理することを特徴とする請求項 1 又は 2 記載の特性を有する炭素質多孔質体の製造方法。

【請求項 4】 アクリロニトリル系耐炎繊維を主要構成成分とする不織布を不活性雰囲気中 1300℃ 以上の温度で処理した後、熱硬化性樹脂を含浸し、再度不活性雰囲気中 1300℃ 以上の温度で処理することを特徴とする請求項 1 又は 2 記載の特性を有する炭素質多孔質体の製造方法。

【請求項 5】 アクリロニトリル系耐炎繊維を主要構成成分とする不織布をニードルパンチ法及び／又は水流交絡法にて処理したものをを用いることを特徴とする請求項 3 または請求項 4 記載の炭素質多孔質体の製造方法。

【請求項 6】 アクリロニトリル系耐炎繊維製不織布として、繊維長 25～100 mm のアクリロニトリル系耐炎繊維を用いて作成したものをを用いることを特徴とする請求項 4～5 のいずれか 1 項記載の炭素質多孔質材料の製造方法。

【請求項 7】 請求項 1 ないし請求項 3 のいずれか 1 項記載の炭素質多孔質材料よりなる燃料電池用電極材。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は、電極材料、特に固体高分子型燃料電池ガス拡散層として好適な炭素質多孔質体およびその製造方法に関するものである。

## 【0002】

【従来の技術】 固体高分子型燃料電池用の電極には集電機能に加えて電極反応に関与する物質の拡散・透過性が要求される。また、集電体を構成する材料には導電性、ガス拡散・透過性、ハンドリングに耐えるための強度、電極製造時や電極を組んだときの圧縮に耐える強度等が必要とされる。

【0003】 このような固体高分子型燃料電池用の電極材の製法として特開平 9-157052 号公報のように、炭素短繊維から構成されるシート状前駆体に熱硬化性樹脂を含浸させ、炭化する方法があげられる。たとえば 6 mm 長程度にカットされた炭素繊維をポリビニルアルコールなどの結着剤とともに水中に分散し、スクリーンで引き上げるいわゆる抄紙方法でシート状前駆体を形

成したのち、該前駆体をフェノール樹脂溶液中に浸漬し、乾燥、樹脂硬化後に不活性雰囲気 2000℃ 程度的高温で炭化する方法などが一般的である。

【0004】 しかしながら、このような方法で作製された炭化物は使用する炭素繊維の繊維長が短いためにロール等に巻き取るために必要な柔軟性が悪いという問題点があった。さらに、繊維長が短いことに起因して、シート状炭化物の厚み方向の導電性が上げにくかった。また、導電性を上げるため、シート状物の厚み方向に圧縮プレスすると、空孔率が低下し、ガス透過性が悪くなるという問題があった。

## 【0005】

【発明が解決しようとする課題】 本発明は、上記のような問題点を克服し、ガス拡散、透過性、導電性に優れ、さらに柔軟性を有する燃料電池用電極を提供することを目的とする。

## 【0006】

【課題を解決するための手段】 上記課題に鑑み、本発明者らは鋭意検討した結果、実質的に炭素のみからなる厚さ 1 mm 以下 0.05 mm 以上の多孔質シート状物であって、外径 20 cm 以下の円筒状物に巻回しても破壊しないことを特徴とする炭素質多孔質体を開発するに至った。

## 【0007】

【発明の実施の形態】 以下に本発明をさらに詳しく説明する。

【0008】 本発明の炭素質多孔体を固体高分子型燃料電池電極として用いる場合はガスの透過性が要求されるので体積空孔率が 50% 以上であることが好ましい。該炭素質多孔体の製造方法の一例としてはポリアクリロニトリル系耐炎繊維を主要構成成分とする不織布に熱硬化性樹脂を含浸し、不活性雰囲気中 1300℃ 以上の温度で処理することが挙げられる。また、ポリアクリロニトリル系耐炎繊維を主要構成成分とする不織布を不活性雰囲気中 1300℃ 以上の温度で処理した後、熱硬化性樹脂を含浸し、再度不活性雰囲気中 1300℃ 以上の温度で処理することによっても作り得る。

【0009】 ポリアクリロニトリル系耐炎繊維を主要構成成分とする不織布の作成に際し、ニードルパンチ法及び／又は水流交絡法を用いることにより、不織布の厚み方向への配向を高め得るのが好ましい。尚、水流交絡法はニードルパンチ法に比べて繊維ヘダメージを与えることが少なく、且つ薄物の不織布の作製が可能であり好ましい。

【0010】 (ポリアクリロニトリル系耐炎繊維について) 本発明に用いられるポリアクリロニトリル系耐炎繊維は単糸繊維 0.5～3.3 d t e x のポリアクリロニトリル系繊維を公知の方法で耐炎処理したものが好ましい。また、本発明を実施するに際して用いるポリアクリロニトリル系耐炎繊維不織布の原料としては、上記ポ



リアクリロニトリル系耐炎繊維を巻縮処理し、25～100mm程度にカットしたものを用いるのが好ましい。かくの如き巻縮耐炎化繊維を用いて作成した不織布はニードルパンチ処理、水流交絡処理により繊維間交絡を十分に高めることができる。

【0011】(炭素化方法)耐炎繊維不織布または、樹脂含浸後の耐炎繊維不織布および上記炭素繊維不織布は不活性雰囲気中、高温で処理することで炭素化ができる。その方法は特に限定されないが、例えば以下の方法を用いるのが好ましい。窒素雰囲気中、低温部300℃から高温部800℃まで実質的に直線的な温度勾配を設定した炉に低温部側から一定速度で連続的に前駆体を投入し、高温部側から5分後に取り出し予備炭素繊維不織布を得、引き続き該予備炭素繊維不織布をパッチ式の加熱炉に投入し、窒素雰囲気に置換した後、室温より10℃/minの速度で1300℃以上まで昇温し、且つ所定温度で1時間程度温度を維持した後、10℃/minにて室温まで降温し、炭素化不織布を得る。尚、アクリロニトリル系繊維プレカーサーを不織布作成に使用した場合は、炭素化処理前に耐炎化処理が必要である。予備炭素繊維不織布を炭素化する炉の形式としてはパッチ炉に特に限定されることはなく、連続的に予備炭素繊維不織布を投入し、一定時間の処理を施した後炭素繊維不織布を連続的に取り出す、いわゆる連続炉を使用することも可能である。また、予備炭素化炉と炭素化炉は独立に設置することに限定しているわけではなく、所望の昇温速度を確保できるのであれば、予備炭素化炉と炭素化炉が一体となってもかまわない。また、一旦予備炭素化温度領域の処理を行った後、同一の炉を用いて温度を炭素化温度領域に設定し直して炭素化処理を行ってもかまわない。

【0012】(熱硬化性樹脂および含浸方法について)熱硬化性樹脂は焼成することにより炭化され、それ自身が導電体としての役割を果たすため、炭化収率の高い樹脂を用いるのが好ましい。炭化される化合物としてはポリアクリロニトリル系ポリマー、ポリウレタン系ポリマー、フェノール系樹脂、フラン系樹脂、セルロース系高分子化合物等が挙げられる。本発明に用いる熱硬化性樹脂は常温において粘着性、或いは流動性を示す物で、フェノール系樹脂、フラン系樹脂等が好ましく用いられる。フェノール系樹脂としては、アルカリ触媒存在下にフェノール類とアルデヒド類の反応によって得られるレゾールタイプフェノール樹脂を用いることができる。また、レゾールタイプの流動性フェノール樹脂に、公知の方法によって酸性触媒下にフェノール類とアルデヒド類の反応によって生成する固体の、熱融着性を示すノボラックタイプのフェノール樹脂を溶解混入させることもできるが、この場合は硬化剤、例えばヘキサメチレンジアミンを含有した、自己架橋タイプのものを用いることが好ましい。フェノール類としては、例えば、フェノール、

ル、レゾルシン、クレゾール、キシロール等が用いられる。アルデヒド類としては、例えばホルマリン、パラホルムアルデヒド、フルフラール等が用いられる。また、これらを混合物として用いることもできる。これらはフェノール樹脂として市販品を利用することも可能である。

【0013】本発明に用いる樹脂含浸方法としては特に限定されないが、一般的な方法としてはディップ法、ニップ法があり、樹脂を溶剤等に溶かし粘度調整を行い、次いで耐炎繊維不織布あるいは炭素繊維不織布を樹脂溶液中に潜らせ、次いで余分な樹脂を、絞り装置等で絞る方法である。

【0014】また、ラミネーター等を用い直接樹脂を耐炎繊維不織布又は炭素繊維不織布に塗る方法。あるいは樹脂を一旦フィルム化し、その後耐炎繊維不織布又は炭素繊維不織布に転写する方法。更に樹脂粘度が比較的低い場合はスプレー法も用いることができる。

【0015】

【実施例】以下、実施例により本発明を更に詳細に説明する。

【0016】(外径20cm以下の円筒状物への巻回について)サンプルを外径20cmおよび内径15cmの紙管に密着するよう一周以上巻き付け、切断などの破壊が起こらないかどうか観察した。

【0017】(空気透過率の測定について)通気性テスター FX3300 (テクステスト社製 スイス)を用い、1サンプルについて3回測定し、その平均値を通気度として採用した。測定面積は38cm<sup>2</sup>、空気圧力124Pa一定、単位はcm<sup>3</sup>/(cm<sup>2</sup>・s)で算出した。

【0018】(体積抵抗率の測定について)

1)多孔質電極基材を約30mm×30mmの矩形に切り出す。

2)縦(l)、横(w)の寸法および厚み(t)を定圧ノギスを用いて0.01mm単位で測定する。

3)切り出した多孔質電極基材を10枚積層し、50mm直径、10mm厚の銅板で挟み、圧縮して抵抗計を用いて電極間の抵抗(RΩ)を測定し、下式によって体積抵抗率が最小値になる厚さまで圧縮し求めた。

【0019】

【数1】

$$\text{体積抵抗率}(\Omega \cdot \text{cm}) = R \times l \times w / t \times 10$$

【0020】〔参考例〕

(耐炎繊維、炭素繊維不織布の製造)アクリロニトリルを96mol%、メタクリル酸2mol%、アクリル酸メチル2mol%なるアクリロニトリル系重合体で単糸繊度2.2dtexのプレカーサーを空気雰囲気中、温

度 230℃～280℃で熱処理し密度 1.40 g/cm<sup>3</sup>の耐炎繊維を得た、該繊維を公知の方法で捲縮処理し、カット長 76 mm のステーブルファイバーとし、次いで公知の方法でウェブを作り、予備ニードルパンチ処理を行った後、水流交絡処理を行い不織布を得た。次いで不織布をパッチ式の加熱炉に投入し、窒素雰囲気置換した後、1300℃まで昇温し、且つ同温度で 1 時間程度温度を維持した後、室温まで降温し、炭素繊維不織布を得た。

【0021】〔実施例 1〕フェノール樹脂（フェノライト 5900、大日本インキ化学社製）を脱溶媒後、コーターで離けい紙に塗工し、フェノール樹脂フィルムを得た。次いで参考例で得た目付 120 g/m<sup>2</sup>の炭素繊維不織布に目付 90 g/m<sup>2</sup>のレジフィルムを乗せ、フェノール樹脂を転写した後、レジ転写面を下にしてフッ素加工した鉄板に挟み、温度 160℃、圧力 18 MPa の条件下に 10 分間置き、炭素繊維不織布下面のフェノール樹脂の硬化及び炭素繊維不織布内の空気を除去した。次いで、炭素繊維不織布上面に目付 90 g/m<sup>2</sup>のレジフィルムを乗せ、フェノール樹脂を転写した後、

レジ転写面を上にしてフッ素加工した鉄板に挟み、温度 90℃、圧力 5 MPa の条件下に 2 分間程度置き、次いで圧力を 18 MPa まで上げた後、温度を 170℃まで昇温し、15 分間置き、フェノール樹脂の硬化を行った。続いて、上記中間基材を、窒素ガス雰囲気中にて 2000℃で 1 時間加熱し、炭素化することで電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0022】〔実施例 2〕参考例で得た目付 60 g/m<sup>2</sup>の炭素繊維不織布を使用した以外実施例 1 と同様にして電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0023】〔実施例 3〕参考例で得た目付 120 g/m<sup>2</sup>の炭素繊維不織布をフェノール樹脂（フェノライト 5900、大日本インキ化学社製）の 15 質量%エタノール溶液に浸漬し、引き上げて炭素繊維 100 重量部に

対し、75 重量部附着させ、60℃で 2 時間、減圧乾燥した後、フッ素加工した鉄板に挟んで、170℃、圧力 18 MPa の条件下に 15 分間置き、フェノール樹脂を硬化させた。続いて、上記中間基材を、窒素ガス雰囲気中にて 2000℃で 1 時間加熱し、炭素化することで電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0024】〔実施例 4〕参考例で得た目付 60 g/m<sup>2</sup>の炭素繊維不織布を使用した以外実施例 3 と同様にして電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0025】〔比較例 1〕単糸繊度が 1.1 d tex のポリアクリロニトリル系炭素繊維の繊維束を切断し、平均繊維長が 6 mm の短繊維を得た。次にこの繊維束を水中で解繊し、十分に分散したところにバインダーであるポリビニルアルコールを均一に分散させ、抄紙し、目付 60 g/m<sup>2</sup>の炭素繊維ペーパーを製造した。炭素繊維ペーパーをフェノール樹脂（フェノライト 5900、大日本インキ化学社製）の 15 質量%エタノール溶液に浸漬し、引き上げて炭素繊維 100 重量部に対し、75 重量部附着させ、60℃で 2 時間、減圧乾燥した後、フッ素加工した鉄板に挟んで、170℃、圧力 18 MPa の条件下に 15 分間置き、フェノール樹脂を硬化させた。続いて、上記中間基材を、窒素ガス雰囲気中にて 2000℃で 1 時間加熱し、炭素化することで電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0026】〔比較例 2〕フェノール樹脂を含浸させた炭素繊維ペーパーの硬化条件が圧力 21 MPa、170℃で 15 分であること以外、比較例 1 と同様にして電極基材を得た。得られた電極基材の厚み (mm)、空気透過率 (cm<sup>3</sup>/(cm<sup>2</sup>・s))、体積抵抗率 (Ω・cm)、巻回試験の結果を表 1 に示した。

【0027】

【表 1】

	厚み (mm)	空気透過率 (cm <sup>3</sup> /cm <sup>2</sup> ・s)	体積抵抗率 (Ω・cm)	巻回試験
実施例 1	0.32	10.6	0.078	破壊なし
実施例 2	0.22	15.3	0.100	破壊なし
実施例 3	0.30	10.1	0.081	破壊なし
実施例 4	0.20	14.5	0.089	破壊なし
比較例 1	0.18	18.0	0.120	破壊
比較例 2	0.13	9.3	0.108	破壊

【0028】

【発明の効果】本発明により厚さ方向の導電性に優れ、且つ柔軟で曲げにも強い固体高分子型燃料電池電極基板

に好適なシート状多孔質炭素材を提供できるようになった。

## フロントページの続き

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